Circular Dichroism, XCI[1]

Syntheses and CD of Benzene Derivatives with Several Similar Substituents

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Received January 27, 1989

Key Words: Benzene α-band CD / Electric transition moment / Platt-Petruska rule

Several optically active 1,2-di- and 1,3,5-trisubstituted benzene derivatives have been synthesized, in which one substituent is chiral, the others being methyl, ethyl, or neopentyl. The CD spectra within the α-band can be explained well by making use of Platt and Petruska's *q* values. While introduction of OH at the benzylic position of a substituent inverts the direction of the corresponding electric transition moment vector in the plane of the ring, this has no such influence upon the magnetic transition moment perpendicular to the ring.

Circulardichroismus, XCI[1]. – Synthese und CD von Benzolderivaten mit mehreren ähnlichen Substituenten

Mehrere optisch aktive 1,2-di- und 1,3,5-trisubstituierte Benzolderivate, in denen ein Rest chiral ist, die anderen Methyl, Ethyl oder Neopentyl sind, wurden dargestellt. Die CD-Spektren innerhalb der α-Bande lassen sich unter Verwendung der von Platt und Petruska eingeführten *q*-Werte gut deuten. Während die Einführung von OH in benzylischer Position eines Restes zur Richtungsumkehr des zugehörigen elektrischen Übergangsmoments in der Ringebene führt, hat dies auf das entsprechende magnetische Übergangsmoment senkrecht zum Ring keinen solchen Einfluß.

The first singlet–singlet transition of the benzene chromophore of B_{2u} symmetry is electrically as well as magnetically dipole-forbidden, the 0–0 line does, therefore, not appear in the UV absorption spectrum. Only when the symmetry is lowered either by vibrational distortion of the skeleton or by substitution, intensity for this band may appear, a 0–0 line, however, only in the latter case. In an earlier part of this work we had shown[2] how the CD spectrum is influenced by substitution, by making use of benzene derivatives substituted twice or three times with the same chiral group. Depending on the substitution pattern either the electric or the magnetic transition moment vector can be made exactly zero (for averaging over all conformations), which then simplifies the formula for the rotational strength. In general this is given by the scalar product $R = (\vec{\mu},\vec{m})$ of a polar ($\vec{\mu}$) and an axial vector ($\vec{m}$), leading actually to a pseudo-scalar, i.e. a number which changes sign when either the molecule or the co-ordinate system is reflected into its mirror image.

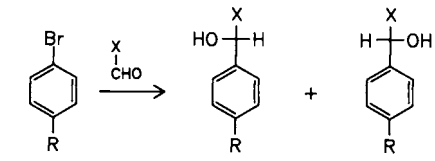
When we are dealing with $\pi \rightarrow \pi^*$ transitions within the π system of the benzene chromophore, any $\vec{\mu}$ lies in the plane of the ring, any $\vec{m}$ is perpendicular to it, so in the first approximation one can write

$$R = \vec{\mu}_{||} \cdot \vec{m}_{st,||} + \vec{\mu}_{st,\perp} \cdot \vec{m}_{\perp}$$

where the subscript || denotes "in plane", ⊥ "perpendicular to the ring", and "st" indicates that this moment has to be stolen from another transition (intra- or interchromophorally). Rotational strength derived from both stolen components $\vec{\mu}_{st}$ and $\vec{m}_{st}$ is too small to be of importance. The electric transition moments (magnitude and direction) can be estimated from so-called *q* values, introduced by Platt[3] and further improved by Petruska[4]. For mono- and differently disubstituted benzene derivatives we had tried also to estimate magnetic transition moments with their help[5], and we have now synthesized some further model compounds analogous to those investigated earlier, where we, however, "cheat" the chromophore by introducing in part achiral ligands showing practically the same *q* values as the chiral ones. (Relevant *q* values: Me: +5.0; Et: +4.5; *i*-Pr: +4.0; CH_2OH: −5.0).

Synthesis of the Model Compounds

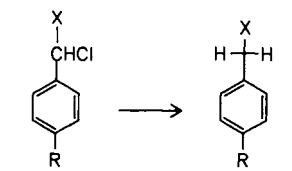
As a chiral substituent we used the same tetramethylcyclopentylcarbinol unit as before[2], the synthon of which is



1a, b, c **2a, b, c** **3a, b**

	R
a	CH_3
b	C_2H_5
c	$CH_2C(CH_3)_3$

X =



4a, b, c **5a, b, c**

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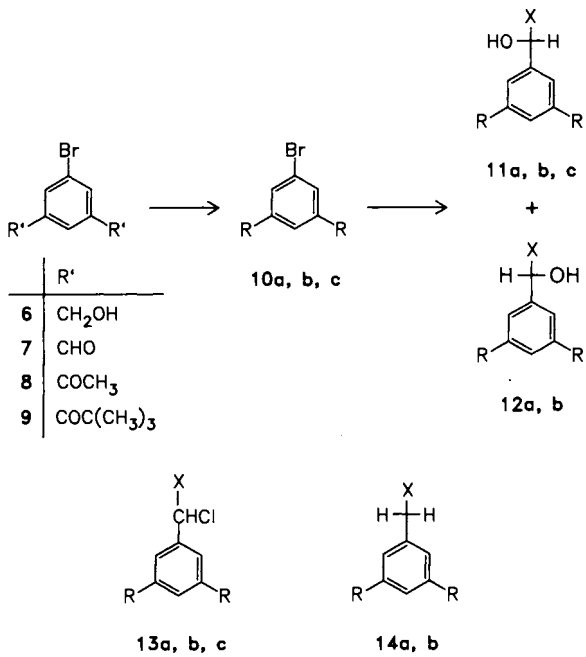
easily available from optically active camphor, or its analogue lacking the OH group. To this end the corresponding Gignard compound, derived from one of the *p*-alkylated bromobenzenes **1a**, **1b**, or **1c**, was treated with aldehyde X-CHO, yielding diastereomeric pairs **2a/3a** or **2b/3b** when starting from **1a** or **1b**, whereas **1c** gave only a single stereoismer **2c**. The absolute configuration at the benzylic carbon was determined from the ^{1}H-NMR spectra making use of the regularities found earlier[2] for such compounds. The hydrocarbons **5a** to **5c** were prepared via the corresponding chloro compounds **4a** to **4c**, whose stereochemistry at the benzylic C was not determined.

For the synthesis of the 1,3,5-trisubstituted benzene derivatives the bromobenzenedimethanol **6** was oxidized with pyridinium chlorochromate to give the dialdehyde **7**, which was treated in turn with the Grignard reagent from methyl iodide or *tert*-butyl bromide. The intermediate benzyl alcohols were not purified but oxidized at once with Jones' reagent to yield the corresponding diketones **8** or **9**. Their carbonyl groups were removed by the Huang-Minlon modification of the Wolff-Kishner reduction to yield the bromo compounds **10b** or **10c** besides some debrominated hydrocarbon. From these or from their dimethyl analogue **10a** the diastereomeric benzyl alcohols **11a**, **b**, **c**, **12a**, and **12b** were prepared via the lithium derivatives, and the three hydrocarbons **14a**, **b**, **c** were obtained in the same way as the *p*-disubstituted compounds just mentioned. **10b** and **10c** also reacted with X-CHO via their Grignard derivatives. The structures of all these substances were established by the usual spectroscopic methods.



CD Spectra and Their Interpretation

A) *Non-ketonic material:* Since the signal/noise ratio of the CD spectra within others than the α band absorption was mostly very bad, only the Cotton effects around 270 nm are discussed in the following.

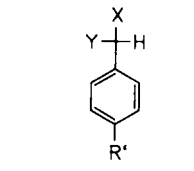
The CD spectra of all compounds are given in Table 1. For reasons discussed earlier[2,6], for a semiquantitative comparison of CD data we can use only the 0–0 line CD and not the rotational strength or $\Delta\varepsilon_{max}$. The chirally monosubstituted benzene derivatives **15** and **16** gave Cotton effect values of −0.12 and −0.46, for this 0–0 line resp.[2], and a priori no decision is possible whether the rotational strength derives from the term with a stolen $\vec{\mu}$, or that with a stolen $\vec{m}$. No doubt arises, however, for **17**, because for symmetry reasons $\vec{m} = 0$, and the measured value[2] of −0.04 is from the term $\vec{\mu}_{||} \cdot \vec{m}_{st,||}$. The best analogue of **17** is **5c**, and its corresponding Δε value is −0.02. This is just what one expects, since $\vec{\mu}$ should not change, whereas, with only one chiral rest instead of two, $\vec{m}_{st}$ can be only half of that for **17**. Furthermore, the CD of **17** is bisignate, whereas that of **5c** is not – again showing the importance to compare only the 0–0 line CDs. The Δε values within the same line of **5a** (−0.012) and **5b** (−0.018) are of the same order of magnitude, as are the *q* values of their alkyl residues **a**, **b**, and **c**, which also differ not much from each other; these Cotton effects are bisignate as well.

Table 1. CD data (isooctane solution)

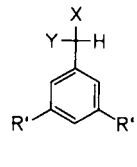
Compound	$\tilde{\nu}$ [cm^{-1}] (Δε)
2a	36620 (+0.052), 37400 (+0.051), 37740s (+0.007), 38190 (+0.026)
2b	36500 (−0.004), 36740 (+0.006), 37430 (+0.008), 37970 (−0.025), 38970 (−0.032)
2c	36390 (−0.014), 37060 (−0.010), 37980 (−0.021), 38870 (−0.016), 39590 (−0.010)
3a	36510 (−0.019), 36900s (−0.007), 37310 (−0.018), 37720s (−0.009), 38100 (−0.010)
3b	36590 (−0.035), 37360 (−0.033), 37810s (−0.017), 38150 (−0.021), 38460 (−0.013)
5a	36300 (−0.012), 36640 (+0.017), 37130 (−0.011), 37550 (+0.005)
5b	36390 (−0.018), 36740 (+0.023), 37300 (−0.011), 37850 (+0.009)
5c	35460 (+0.018), 36500 (−0.009), 36830 (+0.018), 37310 (−0.009), 37670s (+0.007), 37950 (+0.019), 40000 (+0.052)
11a	36270 (−1.020), 37270 (−0.782), 37590s (−0.68), 38240s (−0.44), 38610s (−0.397)
11b	36360 (−1.197), 37340 (−0.995)
11c	36310 (−1.269), 37300 (−1.013)
12a	36220 (+0.626), 37240 (+0.561), 38310s (+0.325)
12b	36280 (+0.802), 37300 (+0.700)
14a	36350 (−0.209), 37410 (−0.174), 38310s (−0.107)
14b	36380 (−0.220), 37340 (−0.166)
14c	36280 (−0.231), 37270 (−0.180)
22	30080 (−2.94), 35240 (−0.62), 41190 (+7.50), 45460s (−3.2), 47570 (−4.53)
23	30210 (−2.11), 35110 (−2.25), 40320s (+4.4), 41250 (+4.7), 46300 (−4.8)

In the case of the *sym*-tris-homochirally substituted products **19** and **20** the first transition is associated with a magnetic, but not with an electric transition moment, and thus distinct 0–0 line absorptions were observed[2] only in the CD spectra (−0.58 and −2.58, resp.), but not in the UV spectra, where only shoulders are detectable at the same wavelength. For **14c**, the closest analogue of **19**, −0.23 is

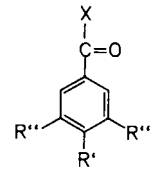
found for the same CD line. The sign is the same as for **19**, and $\Delta\varepsilon$ is nearly 1/3 of the value of **19**; the magnetic transition moment should be the same for both molecules, the missing electric transition moment perpendicular to the aromatic ring of **14c** can be stolen, however, only from one instead of from 3 chiral groups, and so a $\Delta\varepsilon$ value of approximately -0.2 is predicted, in best agreement with the experiment.



	R'	Y
15	H	H
16	H	OH
17	CH_2X	H
18	HO–C(X)–H	OH



	R'	Y
19	CH_2X	H
20	HO–C(X)–H	OH



	R'	R''
21	H	H
22	CH_3	H
23	H	CH_3

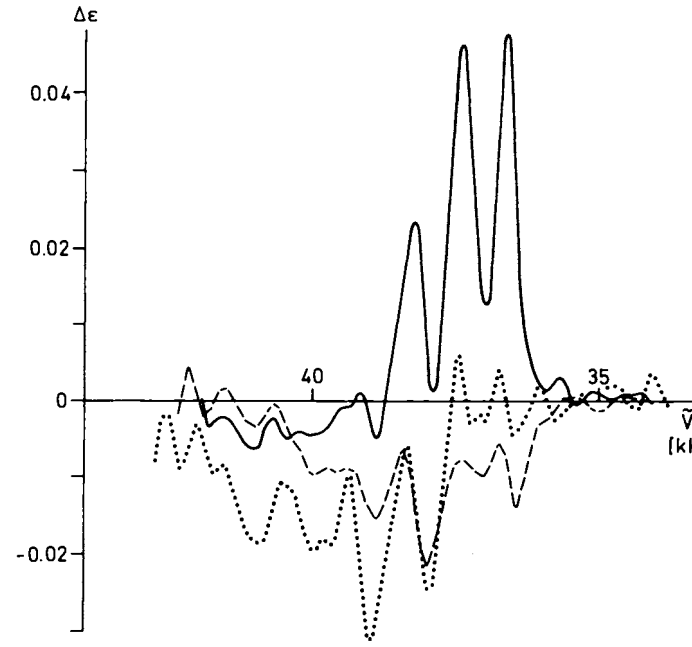


Figure 1. CD of **2a** (———), **2b** (·····), and **2c** (– – –) (all in isooctane solution)

The respective $\Delta\varepsilon$ values for **14a** and **14b** are -0.21 and -0.22, also practically the same. We can thus conclude that in those cases where the substituents are very similar the magnetic transition moment is proportional to the q values, as are the electric transition moments.

For the CH_2OH group the reported q value[4] is -5.0, so its magnitude is the same as that for methyl, but its sign is negative. This means, that the corresponding electric transition moment vector has opposite direction to that of an alkyl group. If the same holds true also for the groups CHROH (R = alkyl), then the electric transition moment vectors will nearly compensate, if we place an alkyl and a CHROH group into *p*-position of a benzene ring. Would $\vec{m}$ be proportional to the q value, then its sign should also be inverted, and we would then expect a CD behaviour similar to that of the *sym*-tris-homosubstituted compounds.

The CD of **2c**, the direct analogue of **18**, has a $\Delta\varepsilon$ value of -0.014, and in this spectrum one can observe a second vibronic series of same sign very distinctly (**18**: $\Delta\varepsilon = -0.04$, another vibronic series is indicated only by a shoulder on the second line). Interestingly enough, mere replacement of the *p*-neopentyl group by a *p*-methyl (**2a**) leads to a positive CD: $\Delta\varepsilon$ within the 0–0 line is here $+0.05$, but the second vibronic series seems to have the same negative sign as for **2c**. This very subtle change of the q value from something between $+4.0$ and $+4.5$ against $+5.0$ has led to a sign inversion!

With the identical chiral substituent present in **2a** and **2c**, $\vec{\mu}$ has obviously changed its direction, the stolen in-plane component of $\vec{m}$ must, however, have remained nearly unchanged. If this explanation is correct, then with a *p*-ethyl group, whose q value is intermediate between that of neopentyl and methyl, we could come close to full compensation of the two individual electric transition moments; indeed in the CD spectrum of **2b** no Cotton effect within the 0–0 line emerges from the noise, only at greater wavenumbers several negative CD lines are detectable. Since the two substituents on the benzene ring are in *p* position and the solutions for the measurements are very dilute, any conformational influence of a *p*-alkyl onto the chiral residue can safely be excluded.

To our knowledge this is the smallest change in substitution on a benzene ring within an achiral ligand, which leads to the inversion of the sign of the CD within the α band. These examples clearly show the determining influence of achiral substituents on an aromatic chromophore upon the CD, a view which we have already expressed more than 15 years ago[7]. They prove furthermore that q values taken from UV spectra are very valuable in CD spectroscopy, too, for prediction of the correlation between chirality and chiroptical properties of aromatic compounds.

The comparison of the CD spectra of **3a** and **3b** with those of their just discussed diastereomers **2a** and **2b** teaches us, however, more about q values. The magnitudes of these q values are determined by the p–π interaction between substituent and the aromatic π system, its sign by the donor or acceptor properties of these rests. q values obtained from UV spectra of simple organic model compounds represent then a weighted average of several conformations; in the CD spectra we might thus expect for the same perturbing group not only different magnitudes, but even different signs within the 0–0 line of the same transition for two different torsional angles around the pivot bond from the benzene ring towards the chiral substituent, and we found in the series of optically active 1,2-disubstituted 1,2-diphenyl ethanes many examples for this effect[6]. We can, therefore, not expect to get similar features in the CD spectra of the mentioned two pairs of diastereomers **2a**/**3a** and **2b**/**3b**. This

would only be the case (in first approximation, neglecting magnitudes of the stolen in-plane component of $\vec{m}$), if the two chiral groups would have the same magnitude of the preferred torsional angle. This is obviously not the case, since both 0–0 line CD values are negative for **3a** and **3b**, and the latter CD is even nearly twice that of the former.

In particular, magnitudes, and even signs of q values for molecules substituted in the benzylic position of ring-closed structures (e.g. a tetralin) must not be the same as those obtained from open-chain model compounds. If, on the other hand, substituents like OR, NR_2, or SR with large q values are present, then these small differences of q values for (substituted) alkyl groups are not important anymore. The CD spectra of simple tetralins, tetrahydroisoquinolines, or isochromanes must, however, take such subtleties into account (cf., e.g., ref.[8]).

The comparison of the CD spectra of the two trisubstituted cmpounds **11c** and **20** with that of **2c** is also highly informative. From the geometry of the benzene ring follows that the overall $\vec{\mu}$ is the same for **2c** and **11c**. Since both have only one and the same chiral substituent, their CD spectra should be alike, if the term $\vec{\mu}_{||} \cdot \vec{m}_{st,||}$ were the governing component of the rotational strength. If, on the other hand, $\vec{m}$ would be proportional to the q value, the in-plane component of $\vec{m}$ for **2c** should be relatively large, which is, however, in contradiction to its very small CD. Since $\Delta\varepsilon$ for the 0–0 line of **11c** is extraordinarily large for such a monochirally-substitued benzene derivative, we have then to conclude that also for **11c** it is the term $\vec{\mu}_{st,\perp} \cdot \vec{m}$, which is the leading one for the rotational strength. This means, then, that the introduction of an OH group into the benzylic position does not (necessarily) change the sign of the $\vec{m}$ of this group.

Keeping this in mind one has to assume that the perpendicular components of $\vec{m}$ of CH_2X and neopentyl are similar, so the overall $\vec{m}$ is of similar magnitude for **11c** and **20**, a $\vec{\mu}$ can, however, be stolen only from one chiral substituent for **11c**, whereas three identical such groups contribute for **20**, and thus sign and magnitude of $\Delta\varepsilon$ within the 0–0 line of **11c** are well-explained, too.

The replacement of a neopentyl by an ethyl group to obtain **11b** can then be predicted to be without great influence onto the chiroptical properties, and indeed the CD within the 0–0 line is nearly the same for both compounds (−1.20 for **11b**). Removing the alkyl substituent from the benzylic positions in the achiral ligands, i.e. by going to **11a**, should also have a moderate effect only, and the corresponding $\Delta\varepsilon$ value drops indeed only to −1.02. For **12a** and **12b**, diastereomeric to **11a** and **11b**, on the basis of the same reasoning as above, no other predictions besides that one can be made, that we expect a relatively large CD. This is indeed found (+0.63 and +0.80, resp.). Inversion at the benzylic carbon atom did lead to a sign inversion of the Cotton effects here.

B) *Ketonic material:* Both substituted compounds **22** and **23** gave within the n→π* absorption a negative Cotton effect of approximately the same magnitude as was found[2] for the non-methylated parent compound **21**. The additional methyl groups should neither influence the preferred conformation of the chiral group, nor will they have any pronounced influence upon the π system of the benzene ring, so this fact is expected. The α band CD is also negative for **22**, **23**, and the reference compound **21**, with $\Delta\varepsilon$ smaller for **23** and larger for **22** than for the standard. Furthermore, within the "conjugation band" and around 210 nm all three CD curves are similar, again in agreement with expectation. Since we have no information about the preferred torsional angles for the two $(O=)C-C_{ar}$ bonds we cannot make predictions for these signs from the structure.

Experimental

Melting points are uncorrected and were determined on a Kofler hot-stage microscope. – ^{1}H-NMR spectra were measured with a Varian T 60 or Bruker WP 80 with tetramethylsilane as internal standard. If not otherwise stated the solvent used was CCl_4. – The IR spectra were taken with a Shimadzu IR-400; CCl_4 as solvent, if not otherwise stated. – Mass spectra were recorded with a Varian CH-5. – The CD spectra were measured with an ISA dichrograph connected on-line to a computer. Curve smothing was performed by using the Golay-Savitzky algorithm (corrected data given by D. Ziessow, *On-line-Rechner in der Chemie*, p. 345, Walter de Gruyter, Berlin 1973). – Elemental analyses are from the micro analysis laboratory of Bochum university. – For thin-layer chromatography, DC alumina foliae, Kieselgel 60 F_{254} from Merck (Darmstadt), were used, staining was done with cerium sulfate/molybdatophosphoric acid reagent. For preparative chromatography, silica gel (50–100 μm) of Macherey-Nagel & Co, Lobar coloumns of type B (Merck), or LiChroprep Si 60 (40– 63 μm) have been used. – Rotations were measured with a polarimeter 141 (Perkin-Elmer) in ethanol. Concentrations are given in g/100 ml.

Compound **1** is commercially available, **2**, **3**, and (1*R*,3*S*)-1,2,2,3-tetramethyl-1-cyclopentanecarboxaldehyde were prepared according to the literature.

Grignard Reaction of **1a**, **1b**, *and* **1c**: The respective bromide **1**, dissolved in dry THF, was added dropwise to a suspension of Mg in a small amount of the same solvent. Thereafter, the suspension was refluxed for 10 min, cooled to room temp., and an equimolar amount of the aldehyde derived from *d*-camphor, dissolved in THF, was added dropwise. After refluxing for 1 h saturated aqueous ammonium chloride was added in the cold, and the organic material was extracted with ether. After the usual workup the resulting diastereomeric alcohols were separated by coloumn chromatography with petroleum ether/ethyl acetate (40:1).

1-⟨(S)-Hydroxy[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-4-methylbenzene (**2a**): Yield 5.76 g (57%), m.p. 57–58°C (hexane). – ^{1}H NMR: δ = 6.95 (m, 4 arom. H), 4.55 (s, 1 benzylic H), 2.25 (s, 3H, 4-Me), 1.00 (s, 3H, Me), 0.88 (s, 3H, Me), 0.84 (d, 3H, $CHCH_3$), 0.80 (s, 3H, Me). – IR: $\tilde{\nu}$ = 3600, 3450 (OH), 1600 cm^{-1}. – MS: *m/z* = 246 ($M^{+\cdot}$), 121 (M – tetramethylcyclopentyl, 100%). – ORD: $[\alpha]_{589}^{22}$ = +35.7, $[\alpha]_{578}^{22}$ = +38.1, $[\alpha]_{546}^{22}$ = +44.3, $[\alpha]_{436}^{22}$ = +72.0, $[\alpha]_{365}^{22}$ = +109.5 (*c* = 0.21).

$C_{17}H_{26}O$ (246.38) Calcd. C 82.87 H 10.64
Found C 82.5 H 10.6

1-⟨(R)-Hydroxy[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-4-methylbenzene (**3a**): Yield 0.64 g (6%), oil. – ^{1}H NMR: δ = 7.03 (m, 4 arom. H), 4.40 (s, benzylic H), 2.28 (s, 3H, 4-Me), 0.82 (s, 3H, Me), 0.77 (s, 3H, Me), 0.75 (d, 3H, $CHCH_3$), 0.40 (s, 3H, Me). –

IR and MS as for **2a**. – ORD: $[\alpha]_{589}^{22} = +4.0$, $[\alpha]_{578}^{22} = +4.5$, $[\alpha]_{546}^{22} = +5.0$, $[\alpha]_{436}^{22} = +6.8$, $[\alpha]_{365}^{22} = +7.8$ ($c = 1.4$).

$C_{17}H_{26}O$ (246.38) Calcd. C 82.87 H 10.64
Found C 82.3 H 10.8

4-Ethyl-1-⟨(S)-hydroxy[1R,3S)-1,2,2,3-tetramethylcyclopentyl]-methyl⟩benzene (**2b**): Yield 2.87 g (29%), m.p. 77–78°C. – ^{1}H NMR: δ = 7.08 (m, 4 arom. H), 4.75 (s, 1 benzylic H), 2.57 (q, 2H, CH_2CH_3), 1.17 (t, 3H, CH_2CH_3), 1.00 (s, 3H, Me), 0.87 (s, 3H, Me), 0.83 (d, 3H, $CHCH_3$), 0.78 (s, 3H, Me). – IR: $\tilde{\nu}$ = 3600, 3450 (OH), 1600 cm^{-1}. – MS: *m/z* = 260 ($M^{+\cdot}$), 135 (M – tetramethylcyclopentyl, 100%). – ORD: $[\alpha]_{589}^{22} = +60.9$, $[\alpha]_{578}^{22} = +64.0$, $[\alpha]_{546}^{22} = +72.7$, $[\alpha]_{436}^{22} = +122.0$ ($c = 2.45$).

$C_{18}H_{28}O$ (260.40) Calcd. C 83.02 H 10.84
Found C 82.7 H 10.8

4-Ethyl-1-⟨(R)-hydroxy[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]-methyl⟩benzene (**3b**): Yield 0.58 g (6%), oil. – ^{1}H NMR ($CDCl_3$): δ = 7.20 (m, 4 arom. H), 4.60 (s, 1 benzylic H), 2.63 (q, 2H, CH_2CH_3), 1.20 (t, 3H, CH_2CH_3), 0.87 (s, 6H, 2 Me), 0.81 (d, 3H, $CHCH_3$), 0.43 (s, 3H, Me). – IR and MS identical with those of **2b**. – ORD: $[\alpha]_{589}^{22} = +3.0$, $[\alpha]_{578}^{22} = +4.9$, $[\alpha]_{546}^{22} = +6.9$, $[\alpha]_{436}^{22} = +9.7$ ($c = 2.0$).

$C_{18}H_{28}O$ (260.40) Calcd. C 83.02 H 10.84
Found C 82.9 H 10.6

1-⟨(S)-Hydroxy[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-4-neopentylbenzene (**2c**): Yield 1.4 g (28%), m.p. 57–60°C (hexane). – ^{1}H NMR: δ = 7.1 (m, 4 arom. H), 4.76 (s, 1 benzylic H), 2.45 (s, 2H, CH_2-tBu), 0.93 (s, 9H, CH_2-*tBu*), 1.06–0.85 (12H, 4 Me on cyclopentane). – IR: $\tilde{\nu}$ = 3600, 3450 cm^{-1} (OH). – MS: *m/z* = 302 ($M^{+\cdot}$), 287 (M – CH_3), 177 (M – tetramethylcyclopentyl, 100%). – ORD: $[\alpha]_{589}^{22} = +49.5$, $[\alpha]_{578}^{22} = +51.9$, $[\alpha]_{546}^{22} = +58.7$, $[\alpha]_{436}^{22} = +96.6$ ($c = 5.56$).

$C_{21}H_{34}O$ (302.48) Calcd. C 83.38 H 11.33
Found C 83.2 H 11.1

1-⟨(ξ)-Chloro[(1S,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-4-methylbenzene (**4a**): To 1.00 g (4.0 mmol) of **3a** in 35 ml of ether and 1.32 ml of pyridine was added at 0°C with stirring 0.66 ml (8.8 mmol) of $SOCl_2$. After 2 h of stirring at room temp. 20 ml of ether was added, and this solution was washed twice with diluted aqueous HCl and three times with water. Usual workup gave 0.95 g (89%) of an oil, which was not further purified. – ^{1}H NMR: δ = 7.00 (m, 4 arom. H), 4.90 (s, 1 benzylic H). – MS: *m/z* = 268/266 ($M^{+\cdot}$), 69 (100%).

The *4-ethyl* (**4b**) and *4-neopentyl* (**4c**) analogues were prepared in a similar manner with 100% yield.

4-Methyl-1-⟨[(1S,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-benzene (**5a**): A solution of 0.95 g (3.6 mmol) of **4a** and 3.3 ml of *tert*-butyl alcohol in 80 ml of THF was refluxed with 1.3 g (188 mmol) of Li for 2 h. After addition of excess methanol in the cold, 100 ml of water was added. The hexane extract was worked up as usual and gave 0.82 g (100%) of raw material consisting of 3 compounds (TLC); the main product was obtained by medium pressure LC: 0.60 g (73%), m.p. 23°C (hexane). – ^{1}H NMR: δ = 6.83 (s, 4 arom. H), 2.7–2.2 (AB-q, 2 benzylic H), 2.25 (s, 3H, 4-Me), 0.90 (d, 3H, Me), 0.80 (s, 3H, Me), 0.77 (s, 3H, Me), 0.67 (s, 3H, Me). – IR: $\tilde{\nu}$ = 1500, 1450 cm^{-1}. – MS: *m/z* = 230 ($M^{+\cdot}$), 69 (100%). – ORD: $[\alpha]_{589}^{22} = +38.5$, $[\alpha]_{578}^{22} = +40.4$, $[\alpha]_{546}^{22} = +46.0$, $[\alpha]_{436}^{22} = +77.3$, $[\alpha]_{365}^{22} = +119.0$ ($c = 1.2$).

$C_{17}H_{26}$ (230.39) Calcd. C 88.62 H 11.38
Found C 88.8 H 11.6

4-Ethyl-1-⟨[(1S,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩benzene (**5b**): Prepared from 0.3 g (1.1 mmol) of **4b** and 1.5 ml of *tert*-butyl alcohol in 20 ml of THF with 0.5 g (71 mmol) of Li as **5a**. Chromatographic purification gave 157 mg (60%) of a colourless liquid. – ^{1}H NMR: δ = 6.95 (s, 4 arom. H), 2.7–2.3 (AB-q, 2 benzylic H), 2.60 (q, 2H, CH_2CH_3), 1.20 (t, 3H, CH_2CH_3), 0.87 (d, 3H, Me), 0.82 (s, 3H, Me), 0.77 (s, 3H, Me), 0.68 (s, 3H, Me). – IR: $\tilde{\nu}$ = 1600 cm^{-1}. – MS: *m/z* = 244 ($M^{+\cdot}$), 119 (M – five-membered ring). – ORD: $[\alpha]_{589}^{22} = +21.6$, $[\alpha]_{578}^{22} = +24.6$, $[\alpha]_{546}^{22} = +28.7$, $[\alpha]_{436}^{22} = +48.7$, $[\alpha]_{365}^{22} = +74.6$ ($c = 0.4$).

$C_{18}H_{28}$ (244.0) Calcd. C 88.45 H 11.55
Found C 88.4 H 11.4

4-Neopentyl-1-⟨[(1S,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-benzene (**5c**): Prepared from 0.4 g (1.2 mmol) of **4c** and 1.6 g of *tert*-butyl alcohol in 40 ml of THF with 0.7 g of Li (100 mmol) as **5a**. Chromatographic purification gave 0.2 g (55%) of a colourless liquid. – ^{1}H NMR: δ = 6.88 (s, 4 arom. H), 2.75–2.22 (AB-q, 2 benzylic H), 2.40 (s, 2H, CH_2-tBu), 0.92 (s, 9H, CH_2-*tBu*). – IR: $\tilde{\nu}$ = 1495, 1450 cm^{-1}. – MS: *m/z* = 286 ($M^{+\cdot}$), 69 (100%). – ORD: $[\alpha]_{589}^{22} = +52.7$, $[\alpha]_{578}^{22} = +55.3$, $[\alpha]_{546}^{22} = +63.0$, $[\alpha]_{436}^{22} = 107.0$, $[\alpha]_{365}^{22} = +167.0$ ($c = 3.34$).

$C_{21}H_{34}$ (286.48) Calcd. C 88.04 H 11.96
Found C 87.5 H 11.8

5-Bromoisophthalaldehyde (7): 21 g (77 mmol) of dimethyl 5-bromoisophthalate[9] in 150 ml of ether, to which CH_2Cl_2 was added until a clear solution was obtained, was added dropwise to a slurry of 4 g (0.2 mol) of $LiAlH_4$ in 30 ml of dry ether. After reflux for 1 h and cooling to room temp., the suspension was treated with saturated aqueous $MgSO_4$ solution and worked up as usual: 15.1 g (90%) of on oil, which slowly crystallized, m.p. 90–91°C. – ^{1}H NMR ($CDCl_3$): δ = 4.67 (d, 4H, 2 CH_2), 7.40–8.03 (m, 3 arom. H). – IR (KBr): 3300 cm^{-1} (OH). – MS: *m/z* = 218/216 ($M^{+\cdot}$), 187/185 (M – CH_2OH), 91 (100%).

To a solution of 16 g (74 mmol) of pyridinium chromate in 100 ml of CH_2Cl_2 was added 5 g (23 mmol) of **6**, and this solution was refluxed until no more **6** could be detected by TLC (approx. 20 h). After cooling, 100 ml of ether was added, the ether was decanted from the black tar, and the latter was washed several times with more ether. After filtration of the ethereal solution through a 10-cm layer of silica gel, the residue was crystallized from petroleum ether/ethyl acetate, yielding 3.6 g (73%) of colourless crystals, m.p. 124°C. – ^{1}H NMR ($CDCl_3$): δ = 10.00 (s, 2H, CHO), 8.24 (m, 3 arom. H). – IR: $\tilde{\nu}$ = 1690 cm^{-1} (C=O). – MS: *m/z* = 214/212 ($M^{+\cdot}$, 100%), 213/211 (M – H), 185/183 (M – HCO).

$C_8H_5BrO_2$ (213.04) Calcd. C 45.10 H 2.37
Found C 44.8 H 2.6

Synthesis of Diketones **8** *and* **9**: To a dispersion of 0.2 mol of Mg foil in 20 ml of dry ether was added a solution of 0.2 mol of methyl iodide or *tert*-butyl bromide in 20 ml of ether. After initial cooling, the mixture was refluxed for another 2 hours. To the cooled suspension was added 0.05 mol of 7, dissolved in 80 ml of THF. This slurry was then refluxed for 2 h, after cooling saturated aqueous NH_4Cl was added, and the material was worked up as usual. This reaction product was then oxidized with Jones' reagent, whose excess was destroyed after 2 h with 2-propanol. After addition of 50 ml of water the reaction product was worked up as usual.

3-Acetyl-5-bromoacetophenone (**8**): 10.5 g (85%), m.p. 83°C (hexane). – ^{1}H NMR: δ = 8.30 (m, 1H at C-2), 8.10 (m, 2H, H at C-4 and C-6), 2.60 (s, 2 Me). – IR: $\tilde{\nu}$ = 1700 cm^{-1} (C=O). – MS: *m/z* = 242/240 ($M^{+\cdot}$), 227/225 (M – CH_3), 199/197 (M – $COCH_3$), 147 (100%).

$C_{10}H_9BrO_2$ (241.09) Calcd. C 49.82 H 3.76
Found C 49.9 H 3.8

5-Bromo-3-pivaloylpivalophenone (**9**): 3.6 g (22%), m.p. 52–53°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 7.8 (m, 3 arom. H), 1.37 (s, 3 Me, neopentyl). – IR: ṽ = 1690 cm^{-1} (C=O). – MS: *m/z* = 326/324 ($M^{+\cdot}$), 57 (100%).

$C_{16}H_{21}BrO_2$ (325.25) Calcd. C 59.09 H 6.51
Found C 59.0 H 6.7

Preparation of **10b** *and* **10c**: To a solution of 0.2 mol of **8** or **9** in 40 ml of diethylene glycol were added 4.2 ml (86 mmol) of hydrazine hydrate and 4 g (70 mmol) of KOH. After heating under reflux for 1.5 h the reflux condensor was replaced by a Zincke apparatus and the solvent was distilled off, until the temp. in the vessel reached 190°C. After refluxing for another 4 h, water was added after cooling to room temp., the raw material was isolated with ether and was chromatographed (hexane) over silica gel.

5-Bromo-1,3-diethylbenzene (**10b**): 1.8 g (41%) of an oil. – ^{1}H NMR: δ = 7.0 (broad s, 2H at C-4 and C-6), 6.8 (broad s, H at C-2), 2.50 (q, 2H, CH_2CH_3), 1.20 (t, 3H, CH_2CH_3). – IR: ṽ = 1600, 1450 cm^{-1}. – MS: *m/z* = 214/212 ($M^{+\cdot}$), 199/197 (M – CH_3), 185/183 (M – C_2H_5), 133 (M – Br, 100%).

$C_{10}H_{13}Br$ (213.12) Calcd. C 56.36 H 6.15
Found C 56.1 H 6.4

5-Bromo-1,3-dineopentylbenzene (**10c**): 1.4 g (23%), m.p. 89 to 90°C (hexane). – ^{1}H NMR: δ = 7.00 (m, 2H at C-4 and C-6), 6.67 (m, H at C-2), 2.40 (s, 2H, CH_2-tBu), 0.92 (s, 9H, CH_2-*tBu*). – IR: ṽ = 1600, 1565 cm^{-1}. – MS: *m/z* = 298/296 ($M^{+\cdot}$), 283/281 (M – CH_3), 57 (tBu, 100%).

$C_{16}H_{25}Br$ (297.29) Calcd. C 64.64 H 8.48
Found C 64.2 H 8.3

Synthesis of **11a**, **11b**, **11c**, **12a**, *and* **12b**: The bromo compound **10a**, **10b**, or **10c** was dissolved in dry ether under argon and cooled with dry ice/acetone to –78°C, then an equimolar amount of BuLi was added dropwise. The mixture was slowly allowed to come to room temp., then it was cooled again to –78°C and 1 equivalent of the aldehyde X-CHO (dissolved in ether) was added dropwise. After stirring for another 2 h at room temp. the material was worked up as usual and chromatographed on silica gel with petroleum ether/ethyl acetate (40:1).

1-⟨(S)-Hydroxy[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-3,5-dimethylbenzene (*S*-**11a**): Colourless oil (45%). – ^{1}H NMR: δ = 6.82 (m, 3 arom. H), 4.56 (s, benzylic H), 2.25 (s, 6H, 3,5-dimethyl), 1.03 (s, 3H, Me), 0.88 (s, 3H, Me), 0.84 (d, 3H, $CHCH_3$), 0.82 (s, 3H, Me). – IR: ṽ = 3600, 3450 (OH), 1600 cm^{-1}. – MS: *m/z* = 260 ($M^{+\cdot}$), 135 (M – tetramethylcyclopentyl), 117 (135 – H_2O, 100%). – ORD: $[\alpha]_{584}^{22}$ = +49.3, $[\alpha]_{546}^{22}$ = +59.4, $[\alpha]_{436}^{22}$ = +98.0, $[\alpha]_{365}^{22}$ = +143.5 (*c* = 0.83).

$C_{18}H_{28}O$ (260.40) Calcd. C 83.02 H 10.84
Found C 83.2 H 10.9

3,5-Diethyl-1-⟨(S)-hydroxy[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩benzene (*S*-**11b**): Colourless oil (51%). –. ^{1}H NMR ($CDCl_3$): δ = 6.93 (s, 2 arom. H), 6.84 (s, 1 arom. H), 4.84 (d, benzylic H), 2.60 (q, 2H, CH_2CH_3), 1.23 (t, 3H, CH_2CH_3), 1.08 (s, 3H, Me), 0.95 (s, 3H, Me), 0.88 (s, 3H, Me), 0.84 (d, 3H, $CHCH_3$). – IR: ṽ = 3580, 3500 (OH), 1590 cm^{-1}. – MS: *m/z* = 288 ($M^{+\cdot}$), 163 (M – tetramethylcyclopentyl, 100%). – ORD: $[\alpha]_{589}^{22}$ = +57.1, $[\alpha]_{578}^{22}$ = +59.2, $[\alpha]_{546}^{22}$ = +67.2, $[\alpha]_{436}^{22}$ = +111.4, $[\alpha]_{365}^{22}$ = +165.2 (*c* = 1.49).

$C_{20}H_{32}O$ (288.46) Calcd. C 83.27 H 11.18
Found C 82.8 H 10.8

1-⟨(S)-Hydroxy[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-3,5-dineopentylbenzene (*S*-**11c**): M.p. 107–108°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 6.96 (d, 2 arom. H), 6.80 (t, 1 arom. H), 4.83 (d, benzylic H), 2.46 (s, 2H, CH_2-tBu), 1.08 (s, 3H, Me), 0.96 (s, 3H, Me), 0.89 (s, 9H, CH_2-*tBu*), 0.84 (d, 3H, $CHCH_3$). – IR: ṽ = 3580, 3450 (OH), 1590 cm^{-1}. – MS: *m/z* = 372 ($M^{+\cdot}$), 247 (M – tetramethylcyclopentyl, 100%). – ORD: $[\alpha]_{589}^{22}$ = +50.8, $[\alpha]_{578}^{22}$ = +52.6, $[\alpha]_{546}^{22}$ = +59.7, $[\alpha]_{436}^{22}$ = +99.6, $[\alpha]_{365}^{22}$ = 147.9 (*c* = 1.17).

$C_{26}H_{44}O$ (372.61) Calcd. C 83.80 H 11.90
Found C 83.3 H 12.0

1-⟨(R)-Hydroxy-[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-3,5-dimethylbenzene (*R*-**12a**): Colourless oil (5%). – ^{1}H NMR: δ = 6.83 (m, 3 arom. H), 4.40 (s, benzylic H), 2.26 (s, 6H, 2 Me), 0.85 (s, 3H, Me), 0.80 (d, 3H, $CHCH_3$), 0.75 (s, 9H, 3 Me), 0.48 (s, 3H, Me). – IR and MS identical with those of **11a**. – ORD: $[\alpha]_{589}^{22}$ = +2.7, $[\alpha]_{578}^{22}$ = +2.9, $[\alpha]_{546}^{22}$ = +3.2, $[\alpha]_{436}^{22}$ = +4.4 (*c* = 1.6).

$C_{18}H_{28}O$ (260.40) Calcd. C 83.02 H 10.84
Found C 82.5 H 10.7

3,5-Diethyl-1-⟨(R)-hydroxy-[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩benzene (*R*-**12b**): Colourless oil (2%). – ^{1}H NMR ($CDCl_3$): δ = 6.96 (s, 2 arom. H), 6.85 (s, arom. H), 4.59 (s, benzylic H), 2.60 (q, 2H, CH_2CH_3), 1.23 (t, 3H, CH_2CH_3), 0.88 (s, 3H, Me), 0.81 (s, 3H, Me), 0.81 (d, 3H, $CHCH_3$), 0.45 (s, 3H, Me). – IR and MS identical with those of **11b**.

$C_{20}H_{32}O$ (288.46) Calcd. C 83.27 H 11.18
Found C 82.8 H 11.3

Synthesis of **13a**, **13b**, *and* **13c**: To 1.5 mmol of (*S*)-**11**, dissolved in 0.5 ml of pyridine and 15 ml of ether, was added 0.26 ml (3.6 mmol) of $SOCl_2$. After 2 h at room temp. 10 ml of water was added, and the mixture was worked up as usual, but the chloro compound **13** was not purified further.

1-⟨(ξ)-Chloro[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-3,5-dimethyl benzene (**13a**): 77% yield. – ^{1}H NMR: δ = 6.77 (m, 3 arom. H), 4.85 (s, benzylic H), 2.22 (s, 6H, 2 Me), 1.08 (s, 6H, 2 Me), 0.92 (s, 3H, Me), 0.82 (d, 3H, $CHCH_3$). – MS: *m/z* = 280/278 ($M^{+\cdot}$), 125 (tetramethylcyclopentyl), 69 (100%).

1-⟨(ξ)-Chloro[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-3,5-diethylbenzene (**13b**): 95% yield. – ^{1}H NMR: δ = 6.83 (m, 3 arom. H), 4.92 (s, benzylic H), 2.57 (q, 2H, CH_2CH_3), 1.20 (t, 3H, CH_2CH_3), 1.13 (s, 6H, 2 Me), 0.97 (s, 3H, Me), 0.85 (d, 3H, $CHCH_3$). – MS: *m/z* = 308/306 ($M^{+\cdot}$), 125 (tetramethylcyclopentyl), 69 (100%).

1-⟨(ξ)-Chloro[(1R,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-3,5-dineopentylbenzene (**13c**): 83% yield. – ^{1}H NMR ($CDCl_3$): δ = 6.85 (m, 3 arom. H), 5.02 (s, benzylic H), 2.47 (s, 2H, CH_2-tBu), 0.90 (s, 9H, CH_2-*tBu*), 1.10 (s, 6H, 2 Me), 0.95 (s, 3H, Me), 0.80 (d, 3H, $CHCH_3$). – MS: *m/z* = 392/390 ($M^{+\cdot}$), 125 (tetramethylcyclopentyl, 100%), 69 (80%).

Synthesis of **14a**, **14b**, *and* **14c**: These were performed as described for the analogues **5**.

3,5-Dimethyl-1-⟨[(1S,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-benzene (**14a**): 59% yield, m.p. 46°C (hexane). – ^{1}H NMR: δ = 6.65 (s, 3 arom. H), 2.23 (s, 6H, 2 Me), 2.67–2.23 (AB-q, 2 benzylic H), 0.87 (d, 3H, $CHCH_3$), 0.83 (s, 3H, Me), 0.77 (s, 3H, Me), 0.67 (s, 3H, Me). – IR: ṽ = 1600 cm^{-1}. – MS: *m/z* = 244 ($M^{+\cdot}$), 69 (100%). – ORD: $[\alpha]_{589}^{22}$ = +40.0, $[\alpha]_{578}^{22}$ = +41.9, $[\alpha]_{546}^{22}$ = +47.6, $[\alpha]_{436}^{22}$ = +80.3, $[\alpha]_{365}^{22}$ = +123.0 (*c* = 2.9).

$C_{18}H_{28}$ (244.40) Calcd. C 88.45 H 11.55
Found C 88.6 H 11.4

3,5-Diethyl-1-⟨[(1S,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩-benzene (**14b**): 80% yield, m.p. 22°C (hexane). – ^{1}H NMR ($CDCl_3$): δ = 6.80 (s, 3 arom. H), 2.66 (q, 2H, CH_2CH_3), 1.20 (t, 3H, CH_2CH_3),

2.80–2.30 (AB-q, 2 benzylic H), 0.87 (d, 3H, $CHCH_3$), 0.82 (s, 3H, Me), 0.78 (s, 3H, Me), 0.69 (s, 3H, Me). – IR: $\tilde{\nu}$ = 1590 cm^{-1} (arom.). – MS: *m/z* = 272 ($M^{+\cdot}$), 147 (M – tetramethylcyclopentyl), 69 (100%). – ORD: $[\alpha]_{584}^{22}$ = +35.9, $[\alpha]_{578}^{22}$ = +37.4, $[\alpha]_{546}^{22}$ = +42.6, $[\alpha]_{436}^{22}$ = +72.2, $[\alpha]_{365}^{22}$ = +111 (*c* = 2.07).

$C_{20}H_{32}$ (272.46) Calcd. C 88.16 H 11.84
Found C 88.3 H 11.5

3,5-Dineopentyl-1-⟨[(1S,3S)-1,2,2,3-tetramethylcyclopentyl]methyl⟩benzene (**14c**): 71% yield, m.p. 62–63° (hexane). – ^1H NMR ($CDCl_3$): δ = 6.73 (s, 3 arom. H), 2.45 (s, 2H, CH_2-tBu), 2.80–2.20 (AB-q, 2 benzylic H), 0.90 (s, 9H, CH_2-*tBu*), 0.87 (d, 3H, $CHCH_3$), 0.82 (s, 3H, Me), 0.78 (s, 3H, Me). – IR: $\tilde{\nu}$ = 1600 cm^{-1}. – MS: *m/z* = 356 ($M^{+\cdot}$), 341 (M – CH_3), 125 (tetramethylcyclopentyl), 69 (100%). – ORD: $[\alpha]_{589}^{22}$ = +27.6, $[\alpha]_{578}^{22}$ = +28.8, $[\alpha]_{546}^{22}$ = +32.7, $[\alpha]_{436}^{22}$ = +55.5, $[\alpha]_{365}^{22}$ = +86.1 (*c* = 1.86).

$C_{26}H_{44}$ (356.60) Calcd. C 87.56 H 12.44
Found C 86.9 H 12.2

CAS Registry Numbers

1a: 106-38-7 / **1b**: 1585-07-5 / **1c**: 51991-28-7 / **2a**: 120173-32-2 / **2b**: 120173-33-3 / **2c**: 120173-34-4 / **3a**: 120292-83-3 / **3b**: 120292-84-4 / **4a**: 120173-35-5 / **4b**: 120173-36-6 / **4c**: 120173-37-7 / **5a**: 120173-38-8 / **5b**: 120173-39-9 / **5c**: 120173-40-2 / **6**: 51760-22-6 / **7**: 120173-41-3 / **8**: 120173-42-4 / **9**: 120173-43-5 / **10a**: 556-96-7 / **10b**: 90267-03-1 / **10c**: 120173-44-6 / **11a**: 120173-45-7 / **11b**: 120173-46-8 / **11c**: 120173-47-9 / **12a**: 120292-85-5 / **12b**: 120292-86-6 / **13a**: 120173-48-0 / **13b**: 120173-49-1 / **13c**: 120173-50-4 / **14a**: 120173-51-5 / **14b**: 120173-52-6 / **14c**: 120173-53-7 / **22**: 120173-54-8 / **23**: 120173-55-9 / 1-formyl-1,2,2,3-tetramethylcyclopentane isomer: 120520-42-5 / dimethyl 5-bromoisophthalate: 51760-21-5

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